

Adsorption of Sodium Cryptate on a Mercury/solution Interface

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Investigation of adsorption of macrobicyclic ligand cryptofix 222 with cation Na^+ on mercury/water solution interface is performed by measuring the differential capacitance (C, E -) curves. A mercury drop (area 0.017cm^2) formed at the end of hydrophobized glass capillary with an inner diameter $135\mu\text{m}$ served as a working electrode. C, E -curves were measured by PAR EG&G 6310 electrochemical impedance analyzer at frequency 370Hz .

The results of measurements in water solutions of cryptofix 222+0.1M Na_2SO_4 are presented in Fig.1. The structure of cryptofix 222 is shown in this figure too. As it follows from literature macrobicyclic ligands form very stable complexes with alkali and alkali earth cations (cryptates); the complexation runs by inclusion of cations into the molecular cavity. Under experimental conditions sodium cryptate $[\text{Na}^+\subset 222]$ is expected to be almost entirely in the complexed state with Na^+ inside the molecular cage (the value of the stability constant K_s is $7.9 \cdot 10^3 \text{ l/mol}$ [1]). We suppose, that the data on the double layer structure of a mercury electrode under cryptate adsorption are obtained for the first time.

As seen from Fig.1, the cryptate complex has a high surface activity at the mercury/solution interface. It should be mentioned that the region of adsorption is very wide ($\approx 1.6\text{V}$ for 10^{-3}M concentration of $[\text{Na}^+\subset 222]$). For all concentrations the limiting coverage of the electrode surface by adsorbed species is reached. From the shape of adsorption/desorption capacity peaks one can conclude that two-dimensional condensation in the system does not take place. Obviously the electrostatic forces between positively charged species prevent the formation of the adsorbed layer with very strong lateral interactions as in the case of 1-adamantanol [2]. In [3] the value of attraction coefficient a in Frumkin isotherm for cryptofix 222 adsorption was found to be -7 . This means that there are repulsive interactions between adsorbed complex molecules. However so large negative value of attraction coefficient seems to be doubtful.

To obtain adsorption parameters of $[\text{Na}^+\subset 222]$ complexes the experimental data were treated by the regression analysis technique [4]. In the first approximation we supposed that cryptate adsorption follows the model of two parallel capacitors coupled with the Frumkin isotherm. The best agreement between calculated and experimental C, E -curves was found under an assumption, that parameters a and $C_{\theta=1}$ (value of C at a complete coverage of the electrode surface by organic molecules $\theta=1$) are the functions of the potential (Fig.2). Calculated values of adsorption parameters are as follows: $\varphi_m = -0.444\text{V}$, $\ln B_m = 14.13$; $A = RT\Gamma_m = 0.384 \mu\text{J cm}^{-2}$; $a_m = 0.728$; $a_{m1} = -1.47\text{V}^{-1}$; $C_m = 6.55 \mu\text{F cm}^{-2}$; $C_{m1} = 1.344 \mu\text{F cm}^{-2} \text{V}^{-1}$; $C_{m2} = 1.044 \mu\text{F cm}^{-2} \text{V}^{-2}$. Here: φ_m is the potential of maximum adsorption; B_m is the adsorption equilibrium constant at $\varphi=\varphi_m$; Γ_m is the limiting adsorption of organic molecules; R and T have their usual meanings; a_m and a_{m1} are the coefficients of a linear dependence of attraction coefficient on E and C_m , C_{m1} and

C_{m2} are the coefficients of parabolic dependence of $C_{\theta=1}$ on E .

Calculated C, E -curves are presented in the Fig.1 (solid lines). As seen from the figure, obtained values of adsorption parameters provide a satisfactory coincidence of calculated and experimental data.

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References

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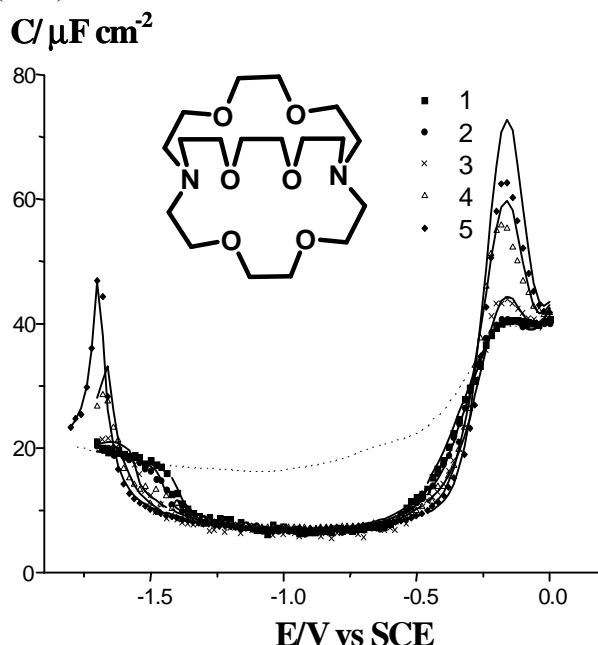


Fig.1. C, E -curves of Hg-electrode in aqueous 0.1M Na_2SO_4 solution (dashed line) and in the presence of complex $[\text{Na}^+\subset 222]$ at the concentrations(M): 1 – 10^{-5} ; 2 – $2 \cdot 10^{-5}$; 3 – 10^{-4} ; 4 – $5 \cdot 10^{-4}$; 5 – 10^{-3} . Points – experimental data; solid lines – calculated data

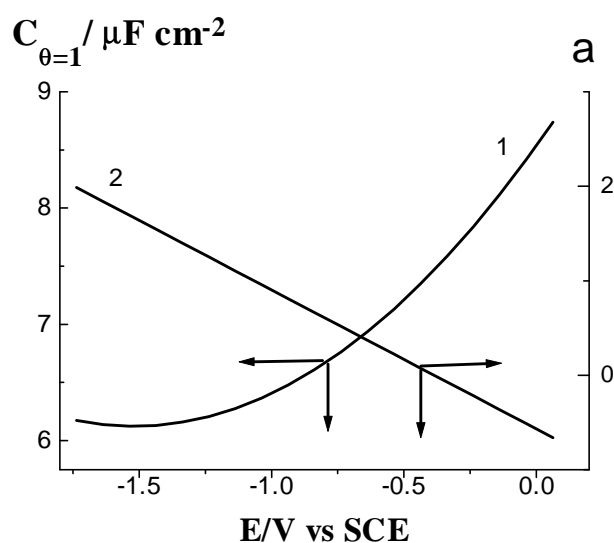


Fig.2. Calculated dependencies of $C_{\theta=1}$ (1) and attraction coefficient (2) on the potential.